

# SCIENCE FOR GLASS PRODUCTION

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## BEHAVIOR OF WATER IN SODIUM AND POTASSIUM BOROSILICATE GLASSES

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IR spectroscopy was used to study the behavior of water in model glasses of the systems  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  and  $\text{K}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ . It was determined that hydroxyl groups and water in molecular form are present in such alkali borosilicate glasses obtained by quenching water-bearing melt. The water distribution between its forms and silicate and borate components of the glass structure depends on their chemical composition. Proton-cation exchange with the participation of non-bridge oxygen atoms and coordinated alkali-metal ions is involved in the process leading to the formation of hydroxyl groups.

**Key words:** borosilicate glasses, water, spectroscopy, structure.

Matrix materials based on borosilicate glass for immobilizing radionuclides become partially saturated with water during production [1 – 3]. The presence of dissolved water is undesirable, because it has a negative effect on the stability of matrix materials during long-term storage [1]. The solution of the problem of increasing the hydrothermal stability of the matrix requires additional study of the interaction of model borosilicate glasses containing water. The state of water in alkali borosilicate glasses obtained by quenching water-containing melt was studied in order to determine the particulars of water behavior in the presence of this interaction.

### EXPERIMENTAL PART

Water-bearing glasses in the systems  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  and  $\text{K}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  with  $\text{M}_2\text{O}/\text{B}_2\text{O}_3 = 1$  ( $\text{M} = \text{Na}, \text{K}$ ) were synthesized and studied. The following reagents were used to synthesize initial water-free glasses: analytical grade  $\text{SiO}_2$ , ultrapure grade  $\text{B}_2\text{O}_3$  and chemical grade  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ . The initial reagents taken in the appropriate proportions were carefully mixed in a porcelain mortar with alcohol, dried at 100 – 150°C and melted in a platinum crucible

in an electric furnace with a nichrome heater at 1200°C. Water-bearing glass was synthesized in 1 cm<sup>3</sup> platinum ampoules by quenching melt. Pre-made glass was comminuted, and a weighed amount of the batch obtained was placed inside an ampoule together with distilled water. The experiments were performed on a high-temperature gas multi-ampoule setup with internal heating and a special apparatus for rapidly shedding pressure and temperature [4]. The duration of the experiments was 4 h, during which time the temperature  $1000 \pm 10^\circ\text{C}$  and pressure  $1500 \pm 50$  bar were maintained. The quenching of the water-bearing melt was conducted by rapidly shedding pressure and temperature. To prevent external factors from having an effect during the experiments the seal tightness of the ampoule was monitored by weighing. The uniformity of the water-bearing glasses was evaluated after optical examination under a microscope.

The total water content in the glasses obtained was determined from their mass change during heating in the platinum crucibles at 1000°C in a furnace with a nichrome heater. The effect of water on the structure of the borosilicate glasses was studied by mid-IR spectroscopy. The distribution of the water between its different forms in the water-bearing glasses obtained was studied by near-IR spectroscopy.

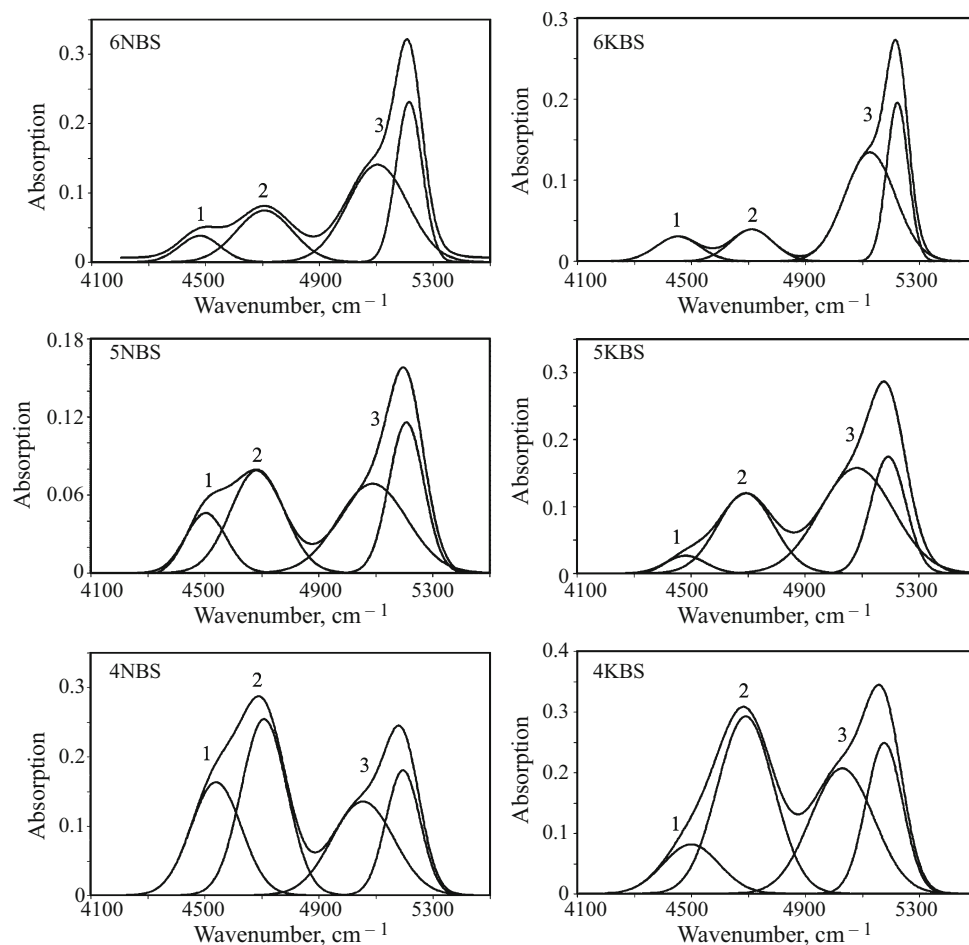
The IR transmission spectra were recorded with a Nexus 870 single-beam IR Fourier spectrometer in the ranges 400 – 1800 cm<sup>-1</sup> (mid-IR range) and 4000 – 8000 cm<sup>-1</sup> (near-IR range). To record the mid-IR spectra the material was mixed with KBr, ground and pressed into a transparent pellet. To record the near-IR spectra 0.2 – 0.5 mm plane-par-

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**Fig. 1.** Near-IR spectra of the synthesized water-containing glasses. The numbers denote the spectral components due to the vibrations of the Si–OH groups in the silicate part of the glass structure (1) and water molecules in the borate (2) and silicate (3) parts of the glass structure.

allel plates, ground and polished on both sides, were fabricated from the glass samples. OMNIC software was used for acquisition and primary processing of the spectra. The band shapes and intensities were determined by subtracting the background and decomposing the bands into Gaussian forms.

## RESULTS AND DISCUSSION

It was established that the solubility of water changes with increasing content of the metaborate component in the experimental sodium and potassium borosilicate glasses (Table 1). In the sodium system these changes are reversible and lie in a narrow range of values. A considerable increase of water solubility was found in the potassium system, and the total water content in 4KBS glass reached 40 wt. %.

All near-IR transmission spectra recorded contain three absorption bands peaking near 4550–4590, 4710–4730 and 5200–5220  $\text{cm}^{-1}$  (Fig. 1). As the metaborate content in the glasses increases the relative intensity of the bands 4550–4590 and 5200–5220  $\text{cm}^{-1}$  decreases and that of 4710–4730  $\text{cm}^{-1}$  increases.

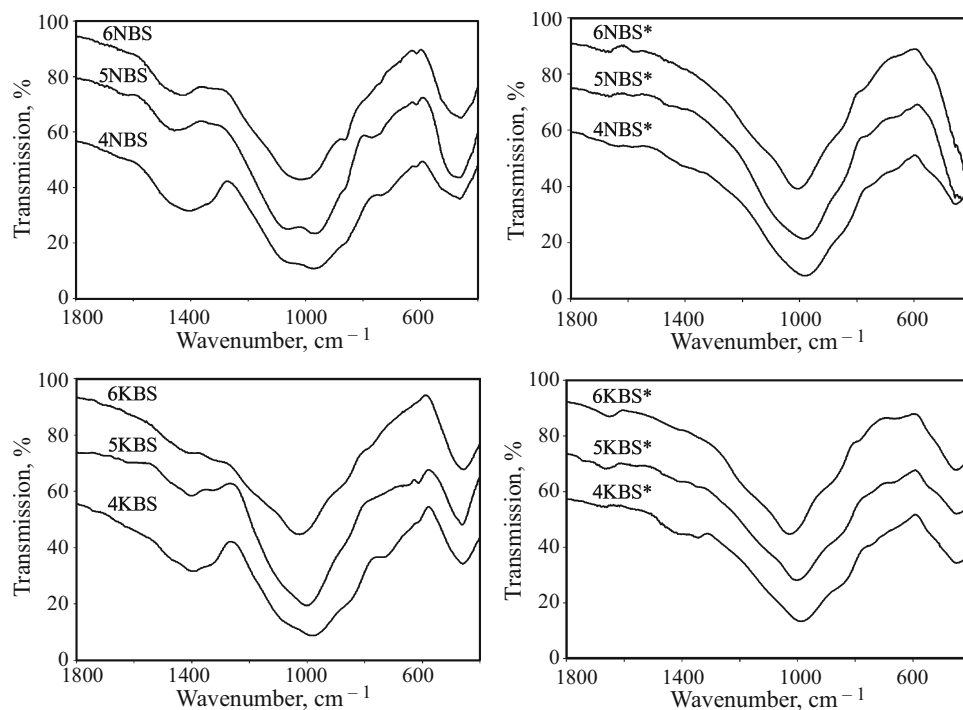
The structural interpretation of the absorption band peaking near 4550–4590  $\text{cm}^{-1}$  is well substantiated [5]. This

band is due to the vibrations of the Si–OH groups in the silicate part of the glass structure. The presence of the 4710–4730  $\text{cm}^{-1}$  band in the IR spectra of previously studied borate glasses, hydrated during a long period of storage in air, made it possible to attribute this band to water dissolved in the molecular form in the borate part of the structure of the borosilicate glasses synthesized.

The 5200–5220  $\text{cm}^{-1}$  band, which dominates in the spectra of all glasses, is characteristic for all water-containing silicate and aluminum-silicate glasses. It is due to the vibrations of the bonds in the water molecule, and its presence

**TABLE 1.** Characteristics of the Synthesized Glasses

Sample	Chemical composition of the initial glass (according to synthesis), mol. %				$\text{H}_2\text{O}$ , wt. %
	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{B}_2\text{O}_3$	$\text{SiO}_2$	
6NBS	20	—	20	60	14.6
5NBS	25	—	25	50	12.9
4NBS	30	—	30	40	14.9
6KBS	—	20	20	60	12.0
5KBS	—	25	25	50	15.3
4KBS	—	30	30	40	40.5



**Fig. 2.** Mid-IR spectra of the synthesized initial water-free and water-containing (\*) glasses.

in the IR-spectra is due to the fact that some of the water in the silicate part of the glass structure is in molecular form [5]. The asymmetry of this band on the low-frequency side is due to the intermolecular interaction of the water molecules with one another and with elements of the anionic structure of the glass. Decomposition of the band  $5200 - 5220 \text{ cm}^{-1}$  into Gaussian lines revealed to components corresponding to bound and free water in the molecular form.

In [6] it is conjectured that the probability of bound hydroxyl groups forming in the alkali-borate glasses is low. This explains the absence in the spectra of the experimental borosilicate glasses of bands associated with hydroxyl groups in the borate part of the glass structure.

The intensity ratio of the bands in the IR spectra indicates that a considerable part of the molecular water dissolves in glass. Irrespective of the total water content, as the metaborate fraction in glass increases the solubility of molecular water in the borate part of the structure increases, which is most strongly manifested in the glass of the potassium system. In glass of the sodium system, this growth is weaker and is accompanied by a decrease in the content of molecular water in the silicate part of the structure.

It was established in [7] that a substantial part of the sodium and potassium ions within the structure of water-free alkali borosilicate glass acts to compensate the charge of the tetra-coordinated boron and non-bridge oxygen bound with silicon in  $\text{SiO}_4$  tetrahedra. On this basis it is supposed that in these glasses the formation of hydroxyl groups as a result of the interaction with water is possible via a mechanism with breaking of bridge bonds as well as via proton-cation exchange with participation of non-bridge oxygen atoms coordinated with sodium and potassium cations, as described in

[8]. To determine the formation mechanism of the hydroxyl groups which is realized in the experimental glasses, the mid-IR spectra of the initial and water-saturated glasses were compared (Fig. 2).

The bands observed in all IR spectra in the ranges  $460 - 480$  and  $1000 - 1100 \text{ cm}^{-1}$  are due to the deformation and asymmetric stretching vibrations of Si-O-Si bonds in complex silicate anions [9]. The band near  $760 - 800 \text{ cm}^{-1}$  is due to the manifestation of symmetric and asymmetric stretching vibrations of Si-O and N-O-B bonds [9]. The absorption in the region  $940 - 980 \text{ cm}^{-1}$  is due to the deformation and asymmetric stretching vibrations of the B-O bond in  $\text{BO}_4$  tetrahedra [10]. The bands peaking near  $720$  and  $1420 \text{ cm}^{-1}$  are due to deformation and stretching vibrations of the B-O bond in  $\text{BO}_3$  triangles [10]. The change in the intensity of IR bands of glasses corresponds to the change in the fraction of these bonds in the glass structure.

Compared with the spectra of the initial glasses the  $980 \text{ cm}^{-1}$  band becomes stronger and the  $1430 \text{ cm}^{-1}$  band weaker in all IR spectra of water-containing glasses. This indicates a decrease in the fraction of  $\text{BO}_3$  triangles in the glass structure and an increase of the fraction of  $\text{BO}_4$  tetrahedra. A change of the coordination of boron and substitution of  $\text{BO}_4$  tetrahedra for  $\text{BO}_3$  triangles are possible only if the distribution of alkali metal cations between the silicate and borate parts of the glass structure changes. A decrease of the fraction of alkali metal cations in the silicate part of the glass structure without any appreciable change in the degree of its polymerization indicates that the formation of hydroxyl groups is associated only with proton-cation exchange with the participation of non-bridge oxygen atoms coordinated by sodium and potassium cations.

## CONCLUSIONS

When borosilicate glass becomes saturated with water the water dissolves in molecular form and with formation of hydroxyl groups. The molecular water in the structure of the experimental borosilicate glasses is represented by two species related with the silicate and borate parts of their structure. The hydroxyl groups are represented only by Si–OH groups in the silicate part of the glass structure. As the amount of the metaborate component in the glass increases, the water fraction dissolved in molecular form only in the borate part of the structure increases. A smaller part of the dissolved water participates in the formation of the hydroxyl groups, and proton-cation exchanges with the participation of non-bridge oxygen atoms coordinated by alkali metal ions is involved in hydroxyl formation.

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